

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-214819

(43)Date of publication of application : 11.08.1998

(51)Int.Cl.

H01L 21/3065

C23F 4/00

(21)Application number : 09-013850 (71)Applicant : SUMITOMO METAL IND LTD

(22)Date of filing : 28.01.1997 (72)Inventor : FUJIWARA TORU

## (54) ELECTRODE PLATE FOR PLASMA ETCHING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an electrode plate for plasma etching with reduced production of particles by using glassy carbon having a lattice constant in a specific range regarding a specific plane of an included crystal.

SOLUTION: The glassy carbon has a structure where graphite crystals dispersedly exists in an amorphous matrix. Fluorocarbon polymer is generated by entrance of fluorine between the graphite crystal layers, and the polymer becomes particles. However, the production of particles can be reduced by forming an electrode plate 10 for plasma etching with glassy carbon having the lattice constant in the range of  $3.450\text{\AA}$  to  $4.500\text{\AA}$ ; regarding the (002) plane of the graphite crystal. The electrode plate 10 is formed by processing the glassy carbon into a

disk having a diameter of 200mm and a thickness of 300mm, forming 1,700 pieces through holes 12 each having a diameter of 0.8mm in the disk, forming an attachment hole 14, then, mirror-processing the surfaces of the disk, thereafter, performing purification processing by using chlorine gas.

## CLAIMS

[Claim(s)]

[Claim 1] Lattice constant  $d_{002}$  about the field (002) of the crystal to contain Electrode plate for plasma etching characterized by consisting of glassy carbon which is the range which is  $3.450\text{\AA}$  -  $4.500\text{\AA}$ .

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode plate for plasma etching with which generating of particle consists of little glassy carbon especially about the electrode plate used for the equipment (plasma etcher) for performing plasma etching.

[0002]

[Description of the Prior Art] The etching interior of a room etc. is equipped with the electrode plate in the dry etching system which used the reactant gas plasma in order that only required thickness might etch the whole surface or the pinpointed location of the thin film formed on the wafer or the wafer front face in manufacture of a semiconductor integrated circuit. When that the reactant of the etching gas and the electrode material by which (1) use is carried out is volatility, (2) electrode materials' not serving as a pollution source of an impurity, and the (3) electrodes itself are etched into the ingredient of the electrode plate used for this plasma etching system, properties, like being etched into homogeneity and (4) electrode materials do not serve as a generation source of particle are required. A poor product will be produced, as a result of protecting the part to etching and etching becoming uneven, when particle adheres on a wafer especially. Therefore, it is an important technical problem to obtain the electrode material used as the generation source of particle.

[0003] JP,62-252942,A indicates using the glassy carbon of a high grade as an ingredient of the electrode plate for plasma etching. Furan system resin with this liquefied official report, phenol system resin, or these mixed resin, Or shaping hardening of what carried out addition mixing of the hardening resin fines of the same class at these liquefied resin is carried out plate-like [ of homogeneity thickness ]. Subsequently, after carrying out the baking carbonization of the resin plate at the temperature of about 800 degrees C under an inert atmosphere and carrying out high grade processing of the glassy carbon further obtained by carrying out graphitization processing and doing in this way at the temperature to 3000 degrees C if needed, it has indicated using it for an electrode plate. the electrode for plasma etching with which this official report consists of manufactured glassy carbon is presenting the homogeneity compact tissue of different three-dimension mesh-like glass structure from a graphite, and possesses adaptation physical properties, such as a high grade, high degree of accuracy, and high chemical stability, -- a purport publication is carried out.

[0004] JP,3-119723,A indicates the electrode plate for plasma etching with which porosity consists of high grade glassy carbon which has 1% or less of organization property with the maximum pore diameter of 1 micrometer or less, and the average pore diameter of 0.7 micrometers or less. With the technique of this official report, it is going to control the number of the particle to generate by setting an average pore diameter to 0.7 micrometers or less, setting the maximum pore diameter to 1 micrometer or less, and making porosity into 1% or less. Moreover, JP,6-128762,A tends to aim at reduction of the particle which generates the field granularity of a vitrified carbon-electrode plate by processing it into less than [ Rmax10micrometer ].

[0005] Each cure against reduction of the particle in these Prior arts is premised on particle occurring when a carbon particle is desorbed from a vitrified carbon-electrode plate. However, even if this invention person had improved under such a premise as a

result of examination, effectiveness sufficient about reduction of generating of particle was not acquired.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the electrode plate for plasma etching with less generating of particle.

[0007]

[Means for Solving the Problem] this invention person traced that the carbonization fluorine system giant molecule generated by the reaction of fluorine system gas, such as trifluoromethane ( $\text{CHF}_3$ ) used as reactant gas for etching, and a vitrified carbon-electrode plate had contributed to generating of particle greatly, as a result of considering the cause of generating of particle wholeheartedly. And so that this invention person may get the vitrified carbon-electrode plate which is hard to make it generate a carbonization fluorine system giant molecule by the reaction with fluorine system reactant gas Lattice constant d002 of a graphite layer structure part [ in / as a result of inquiring wholeheartedly / glassy carbon ] That it is related to extent of particle generating Header, If magnitude of this lattice constant is made into the range of 3.450Å - 4.500Å, it will trace that generating of particle can be reduced more, and it came to complete this invention.

[0008] That is, the electrode plate for plasma etching of this invention is the lattice constant d002 about the field (002) of the crystal to contain. It is characterized by consisting of glassy carbon which is the range which is 3.450Å - 4.500Å.

[0009] Lattice constant d002 For example, it can measure by the approach enacted in the 117th committee of Japan Society for the Promotion of Science. The calculation value which the glassy carbon ingredient which constitutes an electrode plate was specifically ground to a predetermined grain size with the primary standard (silicon), was asked for the diffraction peak about a field (002) with the X-ray diffraction method about the obtained mixed powder, and was asked for the calculation value from the acquired peak from the primary standard can amend, and it can ask for a lattice constant d002.

[0010]

[Embodiment of the Invention] It is the product CF 4 to which the reason a carbon ingredient is applied to the electrode plate of a plasma etcher is reacted and made as for the element (fluorine) and carbon which constitute the reactant gas for plasma etching. It is because it is volatility. However, the gestalt of the reactant generated by the reaction of carbon and a fluorine changes with crystallinity of the carbon which reacts. When carbon is a graphite phase (high crystallinity), the reaction of carbon and a fluorine also comes to generate a carbonization fluorine system macromolecule. Generally glassy carbon contains detailed graphite microcrystal, and has the structure with which it was dotted with the graphite lamellar crystal child in the amorphous matrix. A fluorine invades between this graphite lamellar crystal child's layers, and it is (CF) n. Carbonization fluorine system giant molecules, such as n (CF<sub>2</sub>), were formed, and it was found out that this giant molecule serves as particle.

[0011] When this invention person has this graphite lamellar crystal child's lattice constant d002 (the distance between layers, or spacing) smaller than 3.450Å, While finding out that the reaction of the fluorine which invaded, and a graphite lamellar crystal child's carbon tends to progress, and particle occurs mostly relatively It succeeded in reducing generating of particle by making this lattice constant into 3.450Å or more, and forming the electrode plate for plasma etching with the glassy carbon set as the range of 3.450Å - 4.500Å. On the other hand, electric resistance became excessive and was not able to use the glassy carbon with which this lattice

constant exceeds 4.500A as an electrode plate.

[0012] Phenol resin, furan resin, etc. can be preferably used for the raw material resin for manufacturing glassy carbon. When using phenol resin as a start raw material, after fabricating and hardening phenol resin, it is desirable to make into 1500 degrees C - 2000 degrees C temperature which calcinates in order to obtain glassy carbon. Moreover, when using furan resin as a start raw material, casting and after hardening, it is desirable to calcinate at 1500 degrees C - 2000 degrees C like the case of phenol resin. Like a Prior art, at the low temperature of about 800 degrees C, a lattice constant becomes high too much relatively, and what does not function as an electrode plate is easy to be obtained. Moreover, it is d002 when burning temperature is raised to the temperature near 3000 degrees C. The glassy carbon which becomes small too much relatively and the particle of the giant molecule mentioned above tends to generate comes to be obtained.

[0013] Moreover, this invention person is the lattice constant d002 of the crystal contained in glassy carbon rather than reducing the pore diameter and porosity of glassy carbon by which the conventional proposal was made in order to control generating of particle as a result of an experiment. It found out that to store in the predetermined range was more important. Namely, lattice constant d002 When it was the range which is 3.450A - 4.500A, it was found out that an electrode plate with little generating of particle can be offered as a pore diameter and porosity are comparatively high. The glassy carbon which constitutes the electrode plate for plasma etching according to this invention is a lattice constant d002, even if you may have the maximum pore diameter exceeding 1 micrometer, for example, the path has the maximum pore to about 20 micrometers. If it is the range which is 3.450A - 4.500A, there is little generating of particle. Moreover, even if the porosity of the glassy carbon which constitutes an electrode plate according to this invention may also be over 1%, for example, it has the porosity to about 15%, it is a lattice constant d002. If it is the range which is 3.450A - 4.500A, there is little generating of particle.

[0014]

[Example] Although an example explains this invention more below at a detail, this invention is not limited to this example, and it is a lattice constant d002 by other manufacture approaches, other raw materials, for example, furan resin etc., etc. It is possible to obtain the electrode plate of this invention by manufacturing the glassy carbon whose value is 3.450A - 4.500A.

[0015] Using phenol resin as an example 1 - 4 start raw materials, this was ground in mean particle diameter of 15 micrometers, and hot pressing and hardening were performed in 200 degrees C. It calcinated at each temperature which shows the acquired Plastic solid in Table 1, and the vitrified carbonaceous material was obtained. Incidentally, the porosity of a vitrified carbonaceous material was below 0.020 cc/g (about 3%). Each obtained material was processed into disc-like [ with a diameter / of 200mm /, and a thickness of 3mm ]. After having formed 1700 through tubes with a diameter of 0.8mm in the obtained disk, forming the hole for attachment further and carrying out mirror plane processing of the outside surface by wrapping, chlorine gas performed purification processing and the electrode plate was produced. The obtained electrode plate is shown in drawing 1 . The electrode plate 10 for plasma etching is a disk type-like, and many through tubes 12 are formed in the circular field except a periphery. Moreover, the hole 14 for attachment is formed on [ four ] the periphery at the periphery.

[0016] After performing a slip casting and hardening processing, using furan system resin as an example 5 start raw material, it calcinated at 2000 degrees C and the

vittrified carbonaceous material of porosity 0.095 cc/g (about 14%) was obtained. In the vittrified carbonaceous material, the pore which has about 20-micrometer diameter at the maximum was accepted. The obtained vittrified carbonaceous material was processed in the same way as examples 1-4, and the electrode plate for plasma etching was produced.

[0017] The electrode plate was produced like examples 1-4 except having calcinated the Plastic solid, respectively at the temperature shown in one to example of comparison 3 table 1.

[0018] A test piece is cut out from the electrode plate obtained as mentioned above, and it is a lattice constant d002 about glassy carbon. It measured according to the approach enacted in the 117th committee of Japan Society for the Promotion of Science. The result is shown in Table 1. Moreover, a plasma etching system is equipped with the obtained electrode plate, respectively, and they are CHF3 and CF4. And the etching trial was performed for 10 minutes using the reactant gas which mixed Ar. The 6 inch silicon wafer was used for etching. The number of the particle which exists on a wafer was measured with the particle counter after the etching actuation for 10 minutes. The result is shown in Table 1.

[0019]

[Table 1]

[0020] As shown in Table 1, it is the lattice constant d002 of a crystal. The particle occurrences of the examples 1-5 which are within the limits of this invention are sharply reduced compared with the examples 1 and 2 of a comparison. In addition, lattice constant d002 of a crystal In the bigger example 3 of a comparison than 4.5A, since the electric resistance value of an electrode plate was large, it was not able to examine.

[0021]

[Effect of the Invention] As shown above, according to this invention, the electrode plate for plasma etching with less particle generating can be offered. The electrode plate of this invention can bring about stable and uniform etching processing in manufacture of a semiconductor device, and can contribute it to control of a poor product.

---

## TECHNICAL FIELD

[Field of the Invention] This invention relates to the electrode plate for plasma etching with which generating of particle consists of little glassy carbon especially about the electrode plate used for the equipment (plasma etcher) for performing plasma etching.

---

## PRIOR ART

[Description of the Prior Art] The etching interior of a room etc. is equipped with the electrode plate in the dry etching system which used the reactant gas plasma in order that only required thickness might etch the whole surface or the pinpointed location of the thin film formed on the wafer or the wafer front face in manufacture of a semiconductor integrated circuit. When that the reactant of the etching gas and the electrode material by which (1) use is carried out is volatility, (2) electrode materials' not serving as a pollution source of an impurity, and the (3) electrodes itself are

etched into the ingredient of the electrode plate used for this plasma etching system, properties, like being etched into homogeneity and (4) electrode materials do not serve as a generation source of particle are required. A poor product will be produced, as a result of protecting the part to etching and etching becoming uneven, when particle adheres on a wafer especially. Therefore, it is an important technical problem to obtain the electrode material used as the generation source of particle.

[0003] JP,62-252942,A indicates using the glassy carbon of a high grade as an ingredient of the electrode plate for plasma etching. Furan system resin with this liquefied official report, phenol system resin, or these mixed resin, Or shaping hardening of what carried out addition mixing of the hardening resin fines of the same class at these liquefied resin is carried out plate-like [ of homogeneity thickness ]. Subsequently, after carrying out the baking carbonization of the resin plate at the temperature of about 800 degrees C under an inert atmosphere and carrying out high grade processing of the glassy carbon further obtained by carrying out graphitization processing and doing in this way at the temperature to 3000 degrees C if needed, it has indicated using it for an electrode plate. the electrode for plasma etching with which this official report consists of manufactured glassy carbon is presenting the homogeneity compact tissue of different three-dimension mesh-like glass structure from a graphite, and possesses adaptation physical properties, such as a high grade, high degree of accuracy, and high chemical stability, -- a purport publication is carried out.

[0004] JP,3-119723,A indicates the electrode plate for plasma etching with which porosity consists of high grade glassy carbon which has 1% or less of organization property with the maximum pore diameter of 1 micrometer or less, and the average pore diameter of 0.7 micrometers or less. With the technique of this official report, it is going to control the number of the particle to generate by setting an average pore diameter to 0.7 micrometers or less, setting the maximum pore diameter to 1 micrometer or less, and making porosity into 1% or less. Moreover, JP,6-128762,A tends to aim at reduction of the particle which generates the field granularity of a vitrified carbon-electrode plate by processing it into less than [ Rmax10micrometer ].

[0005] Each cure against reduction of the particle in these Prior arts is premised on particle occurring when a carbon particle is desorbed from a vitrified carbon-electrode plate. However, even if this invention person had improved under such a premise as a result of examination, effectiveness sufficient about reduction of generating of particle was not acquired.

---

## EFFECT OF THE INVENTION

---

[Effect of the Invention] As shown above, according to this invention, the electrode plate for plasma etching with less particle generating can be offered. The electrode plate of this invention can bring about stable and uniform etching processing in manufacture of a semiconductor device, and can contribute it to control of a poor product.

---

## TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the electrode plate for plasma etching with less generating of particle.

---

## MEANS

---

[Means for Solving the Problem] this invention person traced that the carbonization fluorine system giant molecule generated by the reaction of fluorine system gas, such as trifluoromethane ( $\text{CHF}_3$ ) used as reactant gas for etching, and a vitrified carbon-electrode plate had contributed to generating of particle greatly, as a result of considering the cause of generating of particle wholeheartedly. And so that this invention person may get the vitrified carbon-electrode plate which is hard to make it generate a carbonization fluorine system giant molecule by the reaction with fluorine system reactant gas Lattice constant d002 of a graphite layer structure part [ in / as a result of inquiring wholeheartedly / glassy carbon ] That it is related to extent of particle generating Header, If magnitude of this lattice constant is made into the range of 3.450Å - 4.500Å, it will trace that generating of particle can be reduced more, and it came to complete this invention.

[0008] That is, the electrode plate for plasma etching of this invention is the lattice constant d002 about the field (002) of the crystal to contain. It is characterized by consisting of glassy carbon which is the range which is 3.450Å - 4.500Å.

[0009] Lattice constant d002 For example, it can measure by the approach enacted in the 117th committee of Japan Society for the Promotion of Science. The calculation value which the glassy carbon ingredient which constitutes an electrode plate was specifically ground to a predetermined grain size with the primary standard (silicon), was asked for the diffraction peak about a field (002) with the X-ray diffraction method about the obtained mixed powder, and was asked for the calculation value from the acquired peak from the primary standard can amend, and it can ask for a lattice constant d002.

[0010]

[Embodiment of the Invention] It is the product CF 4 to which the reason a carbon ingredient is applied to the electrode plate of a plasma etcher is reacted and made as for the element (fluorine) and carbon which constitute the reactant gas for plasma etching. It is because it is volatility. However, the gestalt of the reactant generated by the reaction of carbon and a fluorine changes with crystallinity of the carbon which reacts. When carbon is a graphite phase (high crystallinity), the reaction of carbon and a fluorine also comes to generate a carbonization fluorine system macromolecule. Generally glassy carbon contains detailed graphite microcrystal, and has the structure with which it was dotted with the graphite lamellar crystal child in the amorphous matrix. A fluorine invades between this graphite lamellar crystal child's layers, and it is (CF) n. Carbonization fluorine system giant molecules, such as n (CF<sub>2</sub>), were formed, and it was found out that this giant molecule serves as particle.

[0011] When this invention person has this graphite lamellar crystal child's lattice constant d002 (the distance between layers, or spacing) smaller than 3.450Å, While finding out that the reaction of the fluorine which invaded, and a graphite lamellar crystal child's carbon tends to progress, and particle occurs mostly relatively It succeeded in reducing generating of particle by making this lattice constant into 3.450Å or more, and forming the electrode plate for plasma etching with the glassy carbon set as the range of 3.450Å - 4.500Å. On the other hand, electric resistance became excessive and was not able to use the glassy carbon with which this lattice constant exceeds 4.500Å as an electrode plate.

[0012] Phenol resin, furan resin, etc. can be preferably used for the raw material resin

for manufacturing glassy carbon. When using phenol resin as a start raw material, after fabricating and hardening phenol resin, it is desirable to make into 1500 degrees C - 2000 degrees C temperature which calcinates in order to obtain glassy carbon. Moreover, when using furan resin as a start raw material, casting and after hardening, it is desirable to calcinate at 1500 degrees C - 2000 degrees C like the case of phenol resin. Like a Prior art, at the low temperature of about 800 degrees C, a lattice constant becomes high too much relatively, and what does not function as an electrode plate is easy to be obtained. Moreover, it is d002 when burning temperature is raised to the temperature near 3000 degrees C. The glassy carbon which becomes small too much relatively and the particle of the giant molecule mentioned above tends to generate comes to be obtained.

[0013] Moreover, this invention person is the lattice constant d002 of the crystal contained in glassy carbon rather than reducing the pore diameter and porosity of glassy carbon by which the conventional proposal was made in order to control generating of particle as a result of an experiment. It found out that to store in the predetermined range was more important. Namely, lattice constant d002 When it was the range which is 3.450A - 4.500A, it was found out that an electrode plate with little generating of particle can be offered as a pore diameter and porosity are comparatively high. The glassy carbon which constitutes the electrode plate for plasma etching according to this invention is a lattice constant d002, even if you may have the maximum pore diameter exceeding 1 micrometer, for example, the path has the maximum pore to about 20 micrometers. If it is the range which is 3.450A - 4.500A, there is little generating of particle. Moreover, even if the porosity of the glassy carbon which constitutes an electrode plate according to this invention may also be over 1%, for example, it has the porosity to about 15%, it is a lattice constant d002. If it is the range which is 3.450A - 4.500A, there is little generating of particle.

---

## EXAMPLE

---

[Example] Although an example explains this invention more below at a detail, this invention is not limited to this example, and it is a lattice constant d002 by other manufacture approaches, other raw materials, for example, furan resin etc., etc. It is possible to obtain the electrode plate of this invention by manufacturing the glassy carbon whose value is 3.450A - 4.500A.

[0015] Using phenol resin as an example 1 - 4 start raw materials, this was ground in mean particle diameter of 15 micrometers, and hot pressing and hardening were performed in 200 degrees C. It calcinated at each temperature which shows the acquired Plastic solid in Table 1, and the vitrified carbonaceous material was obtained. Incidentally, the porosity of a vitrified carbonaceous material was below 0.020 cc/g (about 3%). Each obtained material was processed into disc-like [ with a diameter / of 200mm /, and a thickness of 3mm ]. After having formed 1700 through tubes with a diameter of 0.8mm in the obtained disk, forming the hole for attachment further and carrying out mirror plane processing of the outside surface by wrapping, chlorine gas performed purification processing and the electrode plate was produced. The obtained electrode plate is shown in drawing 1 . The electrode plate 10 for plasma etching is a disk type-like, and many through tubes 12 are formed in the circular field except a periphery. Moreover, the hole 14 for attachment is formed on [ four ] the periphery at the periphery.

[0016] After performing a slip casting and hardening processing, using furan system



resin as an example 5 start raw material, it calcinated at 2000 degrees C and the vitrified carbonaceous material of porosity 0.095 cc/g (about 14%) was obtained. In the vitrified carbonaceous material, the pore which has about 20-micrometer diameter at the maximum was accepted. The obtained vitrified carbonaceous material was processed in the same way as examples 1-4, and the electrode plate for plasma etching was produced.

[0017] The electrode plate was produced like examples 1-4 except having calcinated the Plastic solid, respectively at the temperature shown in one to example of comparison 3 table 1.

[0018] A test piece is cut out from the electrode plate obtained as mentioned above, and it is a lattice constant d002 about glassy carbon. It measured according to the approach enacted in the 117th committee of Japan Society for the Promotion of Science. The result is shown in Table 1. Moreover, a plasma etching system is equipped with the obtained electrode plate, respectively, and they are CHF3 and CF4. And the etching trial was performed for 10 minutes using the reactant gas which mixed Ar. The 6 inch silicon wafer was used for etching. The number of the particle which exists on a wafer was measured with the particle counter after the etching actuation for 10 minutes. The result is shown in Table 1.

[0019]

[Table 1]

[0020] As shown in Table 1, it is the lattice constant d002 of a crystal. The particle occurrences of the examples 1-5 which are within the limits of this invention are sharply reduced compared with the examples 1 and 2 of a comparison. In addition, lattice constant d002 of a crystal In the bigger example 3 of a comparison than 4.5A, since the electric resistance value of an electrode plate was large, it was not able to examine.

---

## DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] It is the top view showing the configuration about one example of the electrode plate for plasma etching of following this invention.

[Description of Notations]

10 Electrode Plate for Plasma Etching

12 Through Tube

14 Hole for Attachment